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Synthesis And Characterization of Nanosilver Fluoride Hydroxyapatite

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ABSTRACT
This research aimed to study the characterization of Nanosilver fluoride added with hydroxyapatite solution. This material was developed as an antibacterial agent and remineralizing agent in teeth, by using the properties of nanosilver, fluoride, and hydroxyapatite to overcome problems that commonly occur in the mouth and teeth, namely dental caries caused by bacteria s. mutants. the role of each component, namely, silver nanoparticles act as an antibacterial agent, fluoride ions are used to inhibit tooth demineralization and inhibit bacterial activity, and hydroxyapatite solution acts as the main source of calcium and phosphate ions to assist the remineralization process in teeth. The material was synthesized using three different concentrations of $AgNO_3$ solution 3, 15, and 30 mM. The result is the FT-IR characterization of all samples, the O–H and N–H functional groups appeared only with slight differences in each wavenumber. While PSA indicates the greater the concentration of $AgNO_3$ used in NSF synthesis, the smaller the average particle size, with the results are NSF (3 mM) + hydroxyapatite had an average particle size of 39.636 nm, NSF (15 mM) + hydroxyapatite has an average particle size of 34.974 nm, and NSF 30 ppm + HAp with the average particle size of 34.75 nm.

Keywords—*Nanosilver, fluoride, hydroxyapatite solution, characterization, particle size.*

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1. INTRODUCTION

Dental caries is a disease that often occurs in the oral cavity of living things. Dental caries is the most common oral disease [1]. This occurs due to demineralization of the tooth surface by organic acids derived from carbohydrate fermentation by bacteria and degradation of the organic matrix [2]. The main cause of dental caries is the bacteria *Streptococcus mutans* and *Streptococcus sobrinus*, but *S. mutans* is more cariogenic because it can produce proteins on its cell surface that can help adhere to the tooth surface [3]. Carbohydrates are metabolized by *S. mutans* with lactic acid as the end product where levels of lactic acid cause a decrease in pH in the mouth and cause tooth demineralization [4].

There is no doubt that the fluoride ion contained in toothpaste products can prevent dental caries [5]. The application can be used in a relatively easy way, namely brushing teeth using toothpaste containing fluoride ions to help inhibit tooth demineralization by changing the critical pH for dissolution of minerals in teeth (hydroxyapatite) in bacterial biofilms and adsorption of the surface of the apatite crystals, forming acid-resistant fluoroapatite. with low solubility, besides that fluoride ion also inhibits bacterial activity and acid production from *S. mutans* [6,7].

The antibacterial activity of silver has been known since ancient times where silver can kill various microorganisms at low concentrations and is non-toxic to humans [8,9]. Silver tends to form chemical bonds with compounds containing nitrogen, sulfur, and phosphorus, so it can be said that silver interactions occur in thiol groups on proteins and phospholipid membranes owned by bacteria [10,11]. The effectiveness of the antibacterial properties of silver can be increased by sizing the silver into the nanoparticle scale, where the surface area of the silver nanoparticles can penetrate the bacterial cell wall, change the structure of the cell membrane and even cause cell death. large surface area to volume [12,13]. . Silver

nanoparticles increase cell membrane permeability, generate reactive oxygen species, and interfere with the replication of deoxyribose nucleic acid by releasing silver ions resulting in bacterial death [14].

Hydroxyapatite is a mineral that can be used as an anti-caries product, due to its biocompatible and bioactive properties which are mostly used in medicine and dentistry [1]. Because hydroxyapatite is the main constituent of bones and teeth, where hydroxyapatite when used in products such as toothpaste, in its solid form can help the pores contained in teeth when in the form of solution hydroxyapatite is used as the main source of calcium and phosphate ions so that it can help the process. remineralization of teeth, especially in dental caries caused by *S. mutans* bacteria [6]. Research about silver nanoparticles has become an emerging field in recent years. The first is that silver nanoparticles can be synthesized by reacting their nucleation and growth process, using some different synthetic reagents. Second, the silver nanoparticles have some specifically functionalized with some molecular capping agents, such as proteins. Third, the silver nanoparticles have an antibacterial effect that improves clinical dental treatment. So that Silver nanoparticles can apply to some dentistry as in Figure 1 [12].

Nanosilver fluoride (NSF) added with hydroxyapatite solution was developed as an antibacterial agent and remineralizing agent in teeth consisting of chitosan, silver nanoparticles, fluoride, and hydroxyapatite solution. This agent does not harm human health. This base is expected to prevent tooth decay without the risk of blackening teeth like SDF (sodium diamine fluoride) [15]. This article aims to determine the characteristics of nanosilver fluoride added with hydroxyapatite, which was characterized using FT-IR to determine the functional groups of the synthesized material and characterized using PSA to determine the particle size of the synthesized material.

Figure 1 The antibacterial application of silver nanoparticles in dentistry [12]

2. METHOD

Several instruments used in this research are Fourier Transform Infrared (FT-IR) spectroscopy and Particle Size Analyzer (PSA). Some of the materials used in this study were Chitosan, Aquades, $AgNO_3$, NaF, Glacial acetic acid, $NaBH_4$, and H_3PO_4.

2.1 Solution Preparation

The materials used were $AgNO_3$ 3, 15, and 30 mM solutions which were made by dissolving $AgNO_3$ solids as much as 0.050961 gr, 0.254805 gr, and 0.50961 gr respectively up to 100 mL using distilled water. A 0.5% chitosan solution was prepared by weighing 2.5 grams of chitosan which was then dissolved in a 2% acetic acid solution (10 mL of glacial acetic acid dissolved to 500 mL) and stirred and heated using a magnetic stirrer until completely dissolved. 5000 ppm NaF solution was prepared by dissolving 0.5 gr of NaF dissolved in distilled water up to 100 mL. The hydroxyapatite solution was prepared by dissolving 1 gram of solid hydroxyapatite dissolved in a 5% H_3PO_4 solution.

2.2 NSF synthesis added with hydroxyapatite solution

$AgNO_3$ solution was synthesized on a chitosan medium which was carried out in an ice bath. 50 mL of chitosan was added with 3 mL of $AgNO_3$ solution which was stirred until homogeneous for 10 minutes. Then the solution mixture was reduced with a freshly prepared $NaBH_4$ solution with cold distilled water (0.042 gr, 0.21 gr, and 0.42 gr which were dissolved using distilled water up to 10 mL, each for every $AgNO_3$ solution). The reduction process is carried out by taking 1 mL of the solution which is then added dropwise until it turns dark red. The mixture was then added with 1 mL of 5000 ppm NaF solution and stirred until homogeneous. The solution mixture was then added again with 1% hydroxyapatite solution as much as 3 mL which was then stirred until homogeneous for 30 minutes.

3. RESULT AND DISCUSSION

The synthesis of the silver ion form into nano-sized silver solids with sodium borohydride reducing agent occurs very quickly and the reaction can run uncontrollably so that the size of silver solids (nanoscale) is very quickly exceeded, which is characterized by the appearance of very fast deposits. Sodium borohydride solution must be new because it is easy to react with air so that sodium borohydride can be decomposed into NaOH and must be carried out in an ice bath so that the reaction can be controlled [16]. The presence of chitosan in this synthesis will hold the reduced silver atoms that tend to agglomerate so that they can maintain their size, namely in the nanoscale [13].

Following are the reactions that occur in the synthesis process:

$$2\,AgNO_3\,(aq) + 2\,NaBH_4\,(aq) \rightarrow 2\,Ag\,(s) + H_2\,(g) + B_2H_6\,(g) + NaNO_3\,(aq)$$

3.1. FT-IR Characterization

One of the chemical characterizations is the analysis of functional groups in the synthesized nanosilver-chitosan-fluoride-hydroxyapatite solution. Functional group analysis

using the FT-IR instrument to determine the functional groups of the nanosilver-chitosan-fluoride-hydroxyapatite solution by qualitatively observing the absorbance in infrared light. In addition, characterization with FT-IR has the aim of identifying the type of bonding vibrations between atoms in certain functional groups that will appear at wavenumbers of 4,000-400 cm^{-1}.

Figure 2 shows the FTIR results of Nanosilver-chitosan-Fluoride-Hydroxyapatite with $AgNO_3$ concentrations of 3 mM, 15 mM, and 30 mM. The three FTIR spectra show that the groups that appear are the same group, namely the O–H group and the N–H group. In NSF 3 mM+ Hydroxyapatite the O-H group is shown at a wavenumber of 3326.27 cm^{-1}, while the N-H group appears at a wavenumber of 1634.82 cm^{-1}. While in NSF 15 mM+ Hydroxyapatite the O–H group is shown at a wavenumber of 3325.99 cm^{-1}, while the N–H group appears at a wavenumber of 1634.79 cm^{-1}. And on NSF 30 mM+ Hydroxyapatite the O–H group is shown at

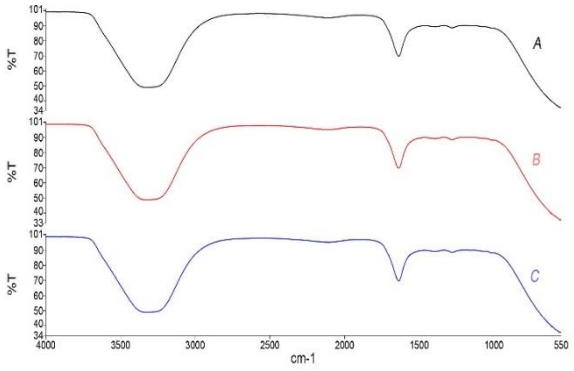

Figure 2. FT-IR analysis results (A) NSF 3 mM + HAp (B) NSF 15 mM + HAp (C) NSF 30 mM + HAp

a wavenumber of 3327.01 cm^{-1}, while the N-H group appears at a wavenumber of 1634.79 cm^{-1}. In these three spectra, the formation of wavenumbers in the range of 3327.01–3325.99 cm^{-1} is caused by the O–H functional group overlapping with the N-H functional group of chitosan [14]. In addition, the wavenumbers in the two functional groups tend to be constant, this happens because there is only a slight difference in the structure and arrangement of molecules which causes the distribution of the absorption peaks to change.

3.2. Particle Size

In measuring particle size, several techniques can be used, one of which is the Particle Size Analyzer (PSA) instrument with laser diffraction technique [16]. This test is one of the quantitative tests to identify the average size of a particle, with the ability to measure up to the order of nanometers. This technique has the principle of scattering laser light by dispersed particles and passing through a laser beam. The results of the scattering consisting of the distribution and the intensity of the scattering will go through a computerized analysis as a result of the particle size distribution [10].

Analysis using the Instrument Particle size analyzer (PSA) was carried out 5 times for each sample, the NSF (3 mM) + hydroxyapatite sample had an average particle size of 39.636 nm (figure 3). While figure 4 showed that the result analysis for sample NSF (15 mM) + hydroxyapatite has an average particle size of 34.974 nm. And the sample NSF (30 mM) + hydroxyapatite solution has an average particle size of 34.75 nm as shown in figure 5. The difference in the average size of each sample indicates that the higher the $AgNO_3$ concentration during the synthesis of Nano Silver Fluoride, the smaller the particle size [17]. These data also indicate that all samples are included in the nanoparticle classification [18].

4. CONCLUSION

Based on the FTIR characterization of all samples, the O–H and N–H functional groups appeared only with slight differences in each wavenumber, indicating very little difference in the structure and arrangement of molecules that caused the distribution of absorption peaks to change. While PSA indicates the greater the concentration of $AgNO_3$ used in NSF synthesis, the smaller the average particle size, with the best results being NSF 30 ppm + hydroxyapatite with an average particle size of 34.75 nm.'

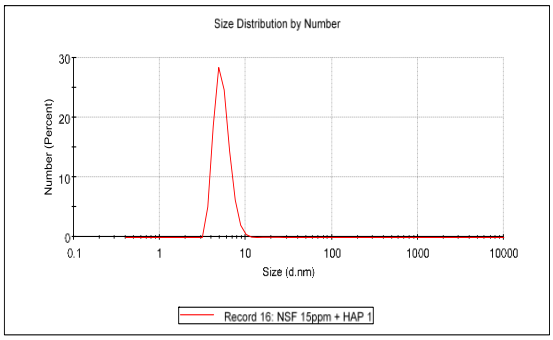

Figure 3. Distribution particle of NSF 3 mM

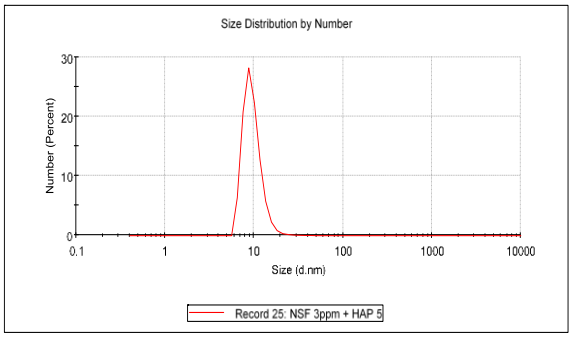

Figure 4. Distribution particle of NSF 15 mM

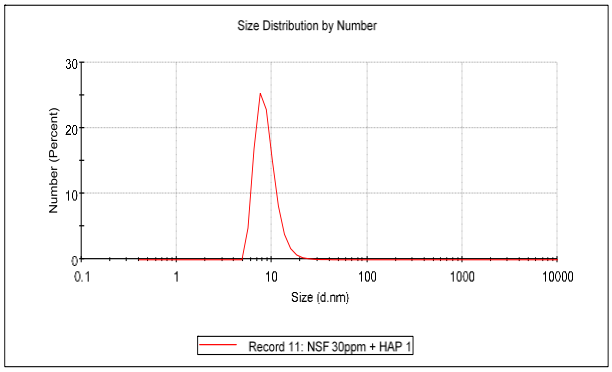

Figure 5. Distribution particle of NSF 30 mM

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